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VOL. 22, SEC. B. NOVEMBER, 1944 NUMBER 6

WETTING POWER IN CALCIUM-SOAP-OIL SYSTEMS[1]

BY WILFRED GALLAY[2] AND IRA E. PUDDINGTON[2]

Abstract

Contact angles of various mineral oils and water on relatively polar and non-polar calcium stearate surfaces prepared by special means were measured. Pre-moistening of the soap surface with small quantities of water decreased the subsequent contact angle against oil. The effect of the polarity of the oil was determined, and the action of water in the system is discussed.

The sedimentation volume of calcium stearate in mineral oil, with and without various added materials, was measured. Water, glycerol, and alcohol effected an agglomeration of the suspended soap, and less polar liquids had no effect. Fatty acid in small quantities brought about a swelling of the soap at room temperature. The relation between wetting power and sedimentation volume is discussed.

Wetting Power

Calcium stearate is poorly wetted by mineral oils, and only small differences are shown in this respect by oils of varying polarity as judged from their viscosity indices. Calcium stearate is not wet by water and even at the boiling point the aqueous suspension of the soap appears to remain entirely unaffected. If, however, water is placed on the soap surface and allowed to drain off, leaving an apparently dry surface, an important alteration in the properties of the surface is brought about. When a mineral oil is subsequently placed on the soap surface previously in contact with water, the oil is then capable of spreading on the soap to a very marked extent. The wetting or spreading tension at the interface is greatly increased.

Since calcium stearate is highly dipolar, with non-polar hydrocarbon chains and a relatively polar calcium carboxylic grouping, the polarity of the soap surface is obviously important. It was attempted therefore to prepare soap surfaces of varying polarity. With a dipolar compound such as stearic acid, this is readily accomplished by melting the material in a glass vessel and allowing it to solidify. The surface thus prepared adjacent to the glass is highly polar whereas the surface formed in contact with air is relatively non-polar, as a result of the orientation of the dipolar molecules. Calcium stearate cannot however be fully melted without decomposition, nor can it be pressed at ordinary temperature to provide suitable surfaces for measurements of the wetting power of liquids.

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Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1228.

[2] *Chemist.*

After some trials, it was found that samples of calcium stearate, after heating to 150° C. for 1 hr. in a glass vessel, could be removed from the container with a smooth surface on the portion adjacent to the glass. These surfaces were presumed to be polar in character. The opposing surfaces of other samples were planed smooth, thus providing what were presumed to be relatively non-polar surfaces.

Wetting power of mineral oils on these surfaces was then determined by contact angle measurements, using the plate method (3). In Tables I and II below, a "dry" surface denotes an untreated surface, as distinguished from "moistened," the latter denoting a soap surface that had been wet with water, and then the water drained off prior to the contact angle measurements. "Polar" and "non-Polar" surfaces refer to the two types of surface mentioned above. Each experiment was repeated several times and the data recorded are averages.

TABLE I

CONTACT ANGLES OF LIQUIDS ON CALCIUM STEARATE

(Surfaces formed in contact with glass and air)

Nature of surface	Liquid	Contact angle, degrees	
		Dry surface	Moistened surface
Polar	500 vis. 95 V.I. oil	57	35
Polar	500 vis. 40 V.I. oil	58	33
Polar	Water	83	—
Non-polar	500 vis. 95 V.I. oil	43	38
Non-polar	500 vis. 40 V.I. oil	45	34
Non-polar	Water	113	—

The differences in polarity of surfaces is shown clearly by the contact angles formed by water. The surface formed in contact with glass is wetted much better by water. Attempts were made at the preparation of "partially polar" surfaces, by cutting diagonally through the soap blocks prepared by heating, and then planing smooth. The contact angle of water on this surface was 114°, and it was therefore concluded that such a surface was essentially the same as the non-polar surface noted above.

Figs. 1 and 2 are photomicrographs of drops of 750 vis. 40 V.I. oil on polar soap surfaces, before and after moistening with water.

The data show that for a given soap surface, oils of high and of low V.I. have virtually the same wetting characteristics. This is true for both dry and moistened surfaces. As might be expected, the mineral oils wet the non-polar soap surfaces appreciably more readily than the polar soap surfaces.

Moistening of the polar soap surface resulted in a reduction of considerable magnitude in the contact angles with oil. The differences are smaller with the non-polar surface because of the initially better wetting power prior to

PLATE I

FIG. 1

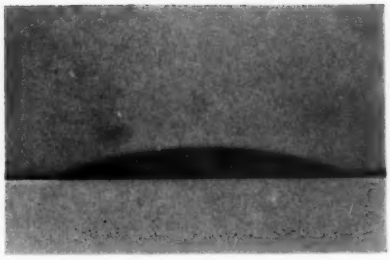

FIG. 2

FIGS. 1 AND 2. *Photomicrographs of drops of 750 vis. 40 V.I. oil on polar soap surface before (Fig. 1) and after (Fig. 2) moistening with water.*

moistening. The contact angles in all cases after moistening are of the same order, indicating that the surfaces have been brought to the same condition regardless of liquid and the initial polarity of the dry surface.

The sorption of water on a calcium soap was determined. A sample of a calcium soap of mixed fatty acids was extracted with petroleum ether. After drying *in vacuo* at 50° C. over phosphorus pentoxide, weighed portions of the soap were exposed to 66% relative humidity in a desiccator. The water sorption after 1, 2, and 21 days, was found to be 3.60, 4.05, and 4.24%, respectively. Under the same conditions, a sample of commercial grade calcium stearate showed an equilibrium sorption of about 2.9%. It is apparent, therefore, that the water take-up of these soaps is appreciable.

The retention of appreciable quantities of water following the moistening and draining of a soap surface is of importance, and the effect was determined by allowing the surface to dry. A pre-moistened surface with one mineral oil, immediately after draining showed a contact angle of 35° C. After the system had stood for two hours in the laboratory, a new contact angle measurement gave a value of 40°, and in a subsequent determination a value of 45° was obtained after a period of about 18 hours. In another instance, two hours' standing brought about an increase in contact angle from 33° to 42°. It is altogether likely that these decreases in wetting power result from the evaporation of water that was retained after moistening and draining.

Since a temperature of 150° C. had been used for the preparation of the soap surfaces, there appeared to be a possibility of minute traces of contamination or of reaction with the surface of the glass. The presence of sodium or potassium on the soap surface might account for part or all of the difference in polarity between the two soap surfaces. Further samples were therefore prepared by heating to 150° C. in contact with pure fused silica and carefully cleaned platinum. These surfaces were chosen for their inertness and as representative of non-polar and polar types. The contact angles of oils and water were then measured on these contact surfaces. The results are shown in Table II.

TABLE II

CONTACT ANGLES OF LIQUIDS ON CALCIUM STEARATE

(Surfaces formed in contact with platinum and silica)

Nature of surface	Liquid	Contact angle, degrees	
		Dry surface	Moistened surface
Polar (platinum)	200 vis. 70 V.I. oil	46	—
Polar (platinum)	500 vis. 40 V.I. oil	47	32
Polar (platinum)	Water	76	—
Non-polar (silica)	500 vis. 40 V.I. oil	45	38
Non-polar (silica)	Water	113	—

It is noted that soap surfaces prepared against platinum yielded results similar to those prepared against glass; in each case the surface was of the more polar type. The danger of contamination against the inert metal is probably negligible. The soap surface formed in contact with silica is relatively non-polar and the contact angle with water is identical with that shown by a soap surface cut through a block. These data corroborate those shown in Table I.

Determinations of the contact angles of water against polar and non-polar stearic acid surfaces yielded values that agreed closely with the numerous data in the literature. The technique of measurement of the contact angles was therefore considered reliable.

The formation of a surface of a polar nature against glass or platinum must involve the exposure of calcium carboxylic groupings on that surface. This polar portion of the soap is wetted more readily by oils containing polar materials than by the more aliphatic type. When the polar soap surface is treated with water, it is probable that the retained water is so orientated as to produce an interfacial tension enabling a greater degree of wetting by oil subsequently placed in contact with the surface.

Sedimentation Volume

The equilibrium sedimentation volume occuped by a finely dispersed solid in lyophobic suspensions has been shown in various systems (1, 2) to be related to the degree of flocculation of the dispersed phase. The effect of water in such systems has been shown to be of particular importance. The extent of agglomeration of the suspended particles is dependent on the surface forces involved. These experiments were extended to suspensions of calcium soaps in oils.

Suspensions of 4 gm. of soap in mineral oil to a total volume of 100 cc. were made up in stoppered graduated cylinders, and after thorough shaking, the soap was allowed to settle. Sedimentation volumes were read at suitable intervals until equilibrium was attained, generally after some weeks of standing. The soap was used in the air-dry condition containing about 2.7% moisture, and also after drying *in vacuo* over phosphorus pentoxide at 50° C. for 48 hr. Observations were made also on the clarity of the supernatant oil during settling. Table III shows results obtained in one series.

The sedimentation volume is increased by moisture in the soap. The agglomeration of the soap is clearly shown also in the settling rates and clarity of the oil. Agglomeration brings about not only an increased equilibrium sedimentation volume, but also a more rapid settling because of increased size of the dispersed units, and an absence of individual particles that otherwise remain dispersed to some extent as a result of convection currents. A decrease in sedimentation volume is obtained with an oil of higher polarity. The addition of a small quantity of water in the last experiment of Table III is shown to have a large effect on the properties of the system.

TABLE III

EFFECT OF WATER ON SEDIMENTATION VOLUME IN CALCIUM-STEARATE–OIL SUSPENSIONS

Soap	Oil	Speed of sedimentation	Clarity of supernatant oil	Sedimentation volume, cc.
Vacuum-dried	300 vis. 95 V.I.	Very slow	Cloudy	12
Vacuum-dried	330 vis. 40 V.I.	Very slow	Cloudy	11
Air-dry	300 vis. 95 V.I.	More rapid	Clear	16
Air-dry	330 vis. 40 V.I.	More rapid	Clear	13.7
Vacuum-dried (+ 0.1 cc. of water)	300 vis. 95 V.I.	More rapid	Clear	20

Further experiments were carried out with varying quantities of added water, and it was shown that a maximum figure is attained for each soap–oil system, beyond which further addition of water yields no further increase in equilibrium settling volume.

The effect of a number of other addition agents was investigated. Suspensions of vacuum-dried calcium stearate in 150 vis. 70 V.I. oil were prepared in 4% concentration, together with the added material noted below. The total volume of the suspension was 50 cc.

TABLE IV

EFFECT OF VARIOUS MATERIALS ON SEDIMENTATION VOLUME IN CALCIUM-STEARATE–OIL SUSPENSIONS

Added material	Speed of sedimentation	Clarity of supernatant oil	Sedimentation volume, cc.
None	Very slow	Cloudy	8
Glycerol, 1 gm.	More rapid	Clear	15
Glycerol, 1 gm.*	More rapid	Clear	29
Stearic acid, 0.25 gm.	Very rapid	Clear	35
Calcium hydroxide, 0.5 gm.	Very slow	Cloudy	8
Ethyl alcohol, 0.15 gm.	Slow	Slightly cloudy	11
Acetone, 0.15 gm.	Very slow	Cloudy	8
Ethyl ether, 0.15 gm.	Very slow	Cloudy	8
Acetic acid, 0.15 gm.	Very rapid	Clear	49
Chloroform, 0.2 gm.	Very slow	Cloudy	8
Carbon tetrachloride, 0.2 gm.	Very slow	Cloudy	8

* *Shaken again after settling, and sedimentation volume redetermined.*

It is noted that glycerol and fatty acid have an effect similar to water in bringing about rapid settling, agglomeration, and larger sedimentation volume. Acetic acid acts similarly through the formation of stearic acid. Added alkali has no apparent effect. Most of the glycerol added in the first determination settled out soon after shaking, and redispersion brought about a large increase in sedimentation volume. The addition of ethyl alcohol

brought about a smaller agglomerating effect, and all other less polar materials used had no effect on the suspension.

Further experiments were carried out on suspensions of vacuum-dried and air-dry soap in mineral oil, some of which were subjected to vacuum in order to remove any air that might have been trapped during the preparation. Sedimentation volume determinations showed that this procedure had no effect on the values obtained.

Acknowledgment

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1. GALLAY, W. and PUDDINGTON, I. E. Can. J. Research, B, 21 : 171-178. 1943.
2. GALLAY, W. and PUDDINGTON, I. E. Can. J. Research, B, 22 : 16-20. 1944.
3. GALLAY, W., PUDDINGTON, I. E., and TAPP, J. S. Can. J. Research, B, 21 : 230-235. 1943.

THE STATE OF DISPERSION OF CALCIUM STEARATE IN MINERAL OILS[1]

By Wilfred Gallay[2] and Ira E. Puddington[2]

Abstract

Calcium stearate undergoes a partial melting to a mesomorphic state at about 100° C., as shown by discontinuities in the density–temperature relation and in differential cooling measurements, and by the onset of plasticity. No surface activity is exhibited by the soap in mineral oil, even in the mesomorphic state. Calcium stearate dispersions in a non-polar mineral oil are essentially lyophobic up to 180° C., whereas the soap is dispersed to a sol in more polar oils at a temperature slightly above the partial melting point.

The viscosity of these dispersions, measured over a range of temperatures in a variable-pressure efflux viscosimeter shows unusual characteristics. A maximum viscosity at intermediate temperatures was found, accompanied by a high degree of dilatancy. The presence of water is shown to lower the viscosity and destroy dilatancy by agglomeration of the dispersed soap.

Physical States of Calcium Stearate

Calcium stearate is a crystalline material, whose lattice structure and dimensions have apparently not been investigated. The soap cannot be completely melted without splitting off calcium carbonate and forming stearone. Calcium stearate is heteropolar and therefore the forces holding the molecules in the lattice must consist of two types, viz., (i) strong polar bonds between calcium carboxylic groupings and (ii) weaker Van der Waal's forces along the length of the hydrocarbon chains. It is not known whether calcium stearate forms a double molecule in the lattice as in the case of sodium stearate, or whether the molecule is orientated in the stretched out form, thus yielding a molecular length approximately equal to a double molecule, in which the two stearate groups are adjacent to each other. In this connection, the structure of lead oleate has been investigated by Trillat (12). He was not able to distinguish between the possible stretched out and folded forms for lead oleate in the solid state, but reached on experimental grounds the conclusion that in the mesomorphic state, the molecules are monomolecular and placed end on end, i.e., polar and non-polar groupings are adjacent to one another. Since it is altogether likely that the double molecule is present in the solid state, as noted for example by wetting experiments (9), there is thus a possibility of a drastic alteration and rearrangement with a change in physical state. It has been stated by Lawrence (10) that calcium stearate does not attain an intermediate plastic state.

In view of the heteropolar nature of calcium stearate, some similarity with sodium soaps (4, 5, 13) in change of state with temperature might be expected. The density–temperature relation was investigated. In view of the fact that

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[2] *Chemist.*

calcium stearate cannot be fully melted without decomposition, measurements were made not on the soap alone, but on suspensions of the soap in various mineral oils. The method used was that previously described for similar sodium soap suspensions (5). The soap was previously dried *in vacuo* at 50° C., and the oils used differed widely in polarity as represented by viscosity indices of 110 and 40. The soap concentration was 20% in all suspensions.

Fig. 1 shows the density–temperature relations with the high V.I. oil. Curves 1, 2, and 3 represent data in successive experiments. In Curve 1 it is noted that the density decreases linearly with temperature until about

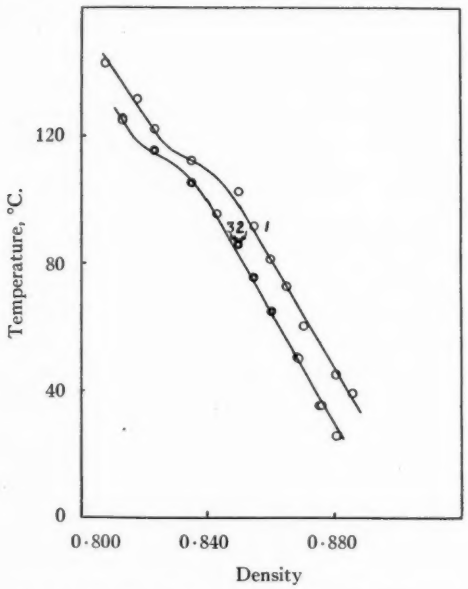

FIG. 1. *Density–temperature relations of 20% calcium stearate in 95 V.I. oil.*

105° C. is reached. There is then a markedly greater decrease in density up to about 120° C., following which the relation is again linear. Vapour was formed by the oil above 140° C., and further measurements were discontinued. In order to check further the possibility of other discontinuities at lower temperatures two further series of measurements were carried out. The data are represented together on Curve 3 of Fig. 1. Here also a relatively sharp decrease in density is shown at about 105° C. and there is no evidence of discontinuities at lower temperatures.

Fig 2 shows the results obtained for the density–temperature relations of calcium stearate in an oil of 40 V.I. The data shown in Curves 1 and 2 were obtained simultaneously. A linear relation is again shown up to about 95 to 100° C., following which there is a greater rate of decrease to about 110° C., with a linear relation again at still higher temperatures.

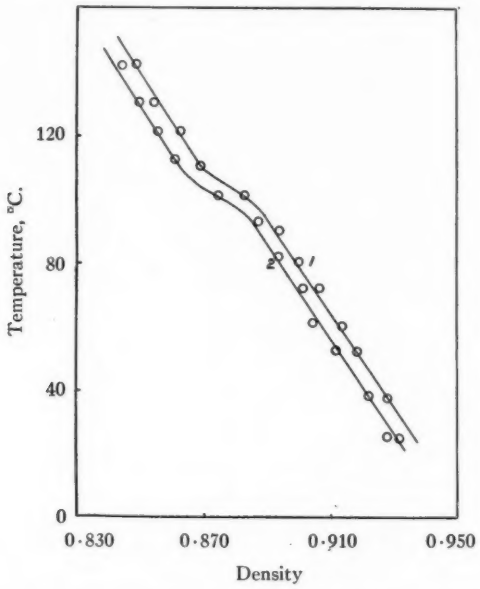

FIG. 2. *Density–temperature relations of 20% calcium stearate in 40 V.I. oil.*

Calcium stearate therefore undergoes a change of state at about 100° C. to a condition of greater volume. The polarity of the suspension medium has only a very minor effect on the temperature at which this alteration occurs. In view of the fact that calcium stearate can be subjected to very much higher temperatures without visual evidence of melting or decomposition, such a discontinuity in molecular volume must be ascribed to a partial melting of the soap. This melting or partial disordering of the lattice is the result of the loosening of the non-polar bonds between the hydrocarbon chains, leaving intact the polar bonds between the calcium-carboxylic groupings. It has previously been shown (4) that sodium stearate has a "bidimensional melting point" at 100° C. This is virtually identical with that found in the present instance with calcium stearate. The hydrocarbon chains above this temperature possess freedom of motion in two dimensions with a consequent sharp increase in molecular volume.

The possibility of other discontinuities was further investigated by means of differential cooling measurements, using the method previously described (4, 5) for sodium soaps. A change in state should be manifested also in corresponding thermal changes. Fig. 3 shows the results obtained on calcium stearate alone in which the temperature differential of the soap and vessel is plotted against the temperature of the soap. It is noted that a sharp break is obtained between 105° C. and 100° C. A second series of measurements

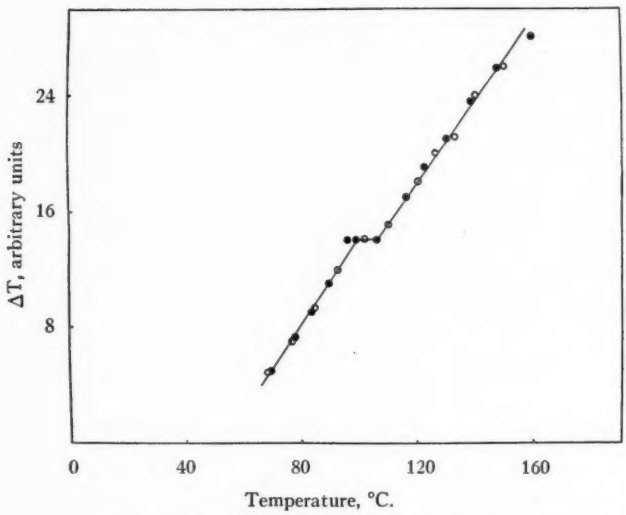

FIG. 3. *Differential cooling curve of pure calcium stearate.*

showed virtually identical results. This corroborates well the evidence obtained in the density–temperature relations.

Fig. 4 shows differential cooling curves for 40% suspensions of calcium stearate in two oils, viz. 110 V.I. and 40 V.I. In the oil of higher V.I. a marked discontinuity was obtained on cooling between 95° C. and 85° C. It would appear that even this relatively highly non-polar medium is effective in reducing slightly the temperature at which the change in state occurs with the soap alone. With the low V.I. oil (Curve 2) there is no indication of a discontinuity of any considerable magnitude. In this connection, the following observations are of interest. When calcium stearate is heated in suspension in a low V.I. oil, there is noted a marked swelling or increase in viscosity of the suspension at about 95° C., and this is followed with little further rise in temperature by a dispersion of the soap to a clear sol. In view of the thermal relations involved in the two processes, viz. (i) solvent effect of the oil and (ii) changes of state in the soap, it appears likely that no break, or a very minor discontinuity only, may be expected in the differential cooling. The two thermal changes may substantially cancel each other. With the oil of high V.I., however, no appreciable solvent effect is obtained until a relatively high temperature is reached, and thus a discontinuity resulting from change in state of the soap in suspension can be observed (Curve 1, Fig. 4).

If a sample of calcium stearate is slowly heated in a test-tube and the crystals are rubbed against the walls of the tube with the end of a thermometer, it is noted that the soap becomes plastic and sticky quite suddenly at a temperature of about 105° C. Plasticity requires a medium for slip or

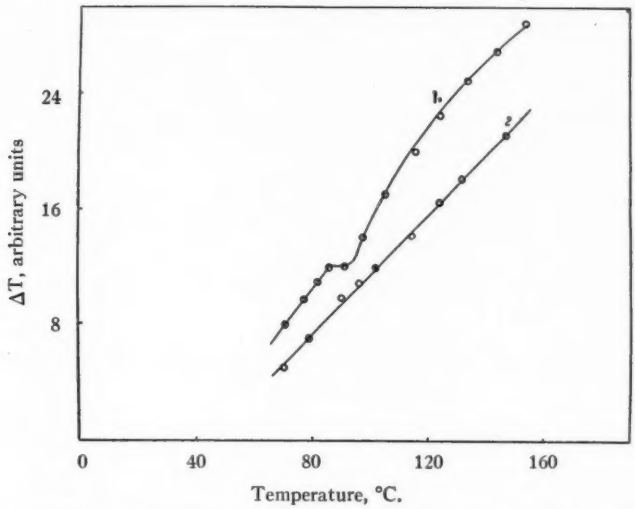

FIG. 4. *Differential cooling curve of 40% of calcium stearate in a 110 V.I. oil (Curve 1) and a 40 V.I. oil (Curve 2).*

distortion in the material and this medium can be provided by the loosened and partially free hydrocarbon chains of the soap, at a temperature where sufficient melting has occurred in these portions of the lattice. This plasticity point is therefore a further corroboration of a change in state of calcium stearate at about 100–105° C.

With sodium stearate (4, 5) discontinuities in the differential cooling curves were obtained at 100° and 125° C. and these were interpreted as bidimensional melting point and plasticity point, respectively. The single discontinuity found with calcium stearate would appear to represent an alteration in physical state corresponding to the attainment of freedom of motion of the hydrocarbon chains, with no large interval in temperature between bidimensional melting and plasticity. Double refraction in the soap disappears also at about 100° C. With regard to the genotypical point, or unidimensional melting point, it was shown with sodium stearate (4) that the effect is so small as to show no apparent discontinuity in the differential cooling curve with the technique used. The same appears to be true with calcium stearate. Whereas detailed precise density measurements with sodium stearate showed changes at 70° C. no such measurements were undertaken with calcium stearate in view of the fact that the soap alone could not be used, and the degree of precision is greatly reduced by suspension in an oil. It may be assumed, however, by analogy with the sodium salt that an initial unidimensional melting occurs at the genotypical point.

Surface Tension of Calcium Stearate in Mineral Oil

Surface tension measurements were carried out on a 1% dispersion of calcium stearate in a 900 vis. 40 V.I. oil. A capillary rise method was used, as described previously for sodium soap dispersions (6). The data are shown in Fig. 5.

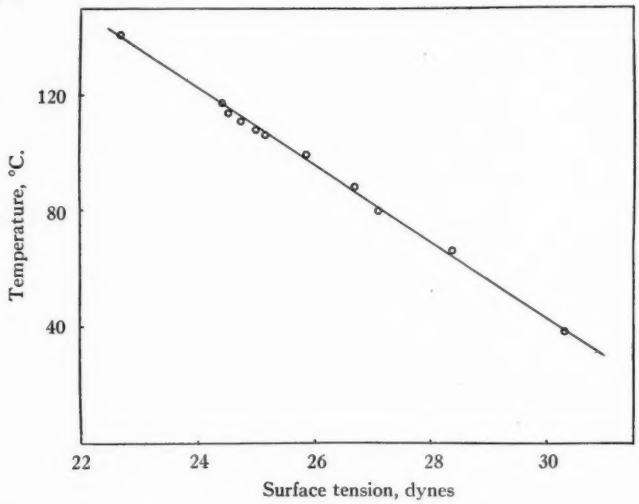

FIG. 5. *Surface tension of a 1% dispersion of calcium stearate in a 900 vis. 40 V.I. oil.*

The measurements were carried out up to 140° C. and it is noted that there is no appreciable discontinuity in the surface tension relation with temperature. The suspension dispersed to a transparent sol at about 107° C. Despite this apparently high degree of dispersion, it would appear that there is no tendency for the soap to concentrate at the oil–air interface, and the surface tension of the dispersion is that of the mineral oil throughout. Changes in physical state with sodium soaps were shown (6) to be accompanied by sudden decreases in surface tension. With calcium stearate, the partial melting at 100° C. brings about no increase in surface activity. This is caused very probably by the difficulties in orientation at the interface, brought about by the two stearate chains attached to each polar calcium carboxylic grouping.

Swelling of Calcium Stearate in Mineral Oils

For the detailed observation of swelling and dispersion in this system, a novel design of heated microscope stage was used, the details of which will be described by one of us elsewhere (11). By means of this apparatus, a small sample of a suspension could be heated to high temperatures, e.g., 200° C., under thermostatic control. The system under observation could also be distorted by means of a fine glass needle in order to observe directly the general type of flow under pressure.

Suspensions of calcium stearate in 10 and 20% concentration in 95 V.I. oil and in 40 V.I. oil were heated in this apparatus up to about 200° C. and observations were made during heating and cooling. In the high V.I. oil, the soap particles appeared quite independent of one another, and on displacement with a fine glass needle, appeared to move past one another with no tendency to adherence. On cooling, some adherence between particles became evident at low temperatures, e.g., 75° C. On continued heating at 175° C. the viscosity of the system decreased, and after cooling the dispersion was a smooth grease. It is altogether likely that considerable oxidation of the oil occurred during the extended heating period, with consequent increase in polarity of the oil.

Suspensions in a low V.I. oil on heating showed considerably less resistance to displacement at higher temperatures, and a much greater plasticity than with the high V.I. oil at lower temperatures.

Viscosity of Calcium Stearate Dispersions

The viscosity of a dispersion of soap in mineral oil is the sum of the viscosity of the free oil and the internal friction brought about by the soap. The soap offers resistance to flow not only by reason of its volume effect, but also as a result of any structure it may form in the dispersion. Variations in viscosity of soap suspensions with temperature offer indications therefore of alterations in the form and state of dispersion of the soap.

The viscosimeter used was of the variable pressure efflux type. It consisted essentially of a reservoir of about 300 cc. capacity leading through a capillary of about 0·25 mm. diameter and 12 cm. length to a small bulb about 1 cm. in diameter and about 5 cc. capacity. The upper and lower limits of this measuring bulb were burnt in with a gold lacquer. Pressure was applied from a compressed air line through an adjacent mercury column blow-off, then through a large surge tank to the viscosimeter. A manometer was placed in the line. Special attachments were provided for cleaning the apparatus and for stirring the contents of the reservoir by means of a stream of air. The viscosimeter was set in an electrically heated and controlled thermostat. The procedure was as follows. The soap suspension was prepared in a separate vessel and transferred to the reservoir. After adjustment of the pressure and allowing time for temperature equilibrium, air pressure was admitted above the suspension in the reservoir, and the time was noted for flow between the marks of the measuring bulb. Prior to the next measurement the suspension which had passed through the capillary was removed by suction, so that fresh non-orientated material was used each time. A series of viscosity measurements were made over a range of pressures at each temperature, with each suspension. Two sizes of capillaries, 0·25 mm. and 1 mm., were used for suspensions of low and of high soap concentrations, respectively.

Viscosity measurements were carried out with a 10% suspension of vacuum dried calcium stearate in a 95 V.I. oil. On heating to about 120° C., a floc-

culation of the soap was observed and the previously finely divided soap separated from the oil to form a soft mass, which rose to the surface. It was not possible to carry out viscosity measurements on the system in this state. On further heating, a gradual redispersion was effected, and a uniform dispersion was obtained at about 180° C. The viscosity was now extremely high, very much higher than with a low V.I. oil. Further heating to 235° C. showed the normal decrease in viscosity resulting from the increased temperature. On cooling, the viscosity increased greatly to a maximum and then the flocculation noted above was again obtained. This cycle is reversible. The soap undergoes a partial melting to the plastic state as described in an earlier section, and the resultant material is then unaffected by the high V.I. oil until a very high temperature is reached. This case is somewhat analogous to that of sodium stearate, which has also been shown (5) to form a reversible lyophobic system in a high V.I. oil.

Viscosity measurements over a range of temperatures were then carried out with suspensions of air-dry calcium stearate in 900 vis. 40 V.I. oil, in concentrations of 3, 10, and 15%. The air-dry soap contained about 3% of water. No difficulties were encountered with agglomeration with the low V.I. oil.

Fig. 6 shows the results obtained with the 3% suspension (small-bore capillary). The viscosity decreases to about 105° C., following which there is a slight increase, followed again by the decrease due to the higher temperature. After the partial melting point, the very low concentration used limits the viscosity increase. On cooling, the curve passes through the maximum at a slightly lower temperature. Throughout this higher viscosity on cooling,

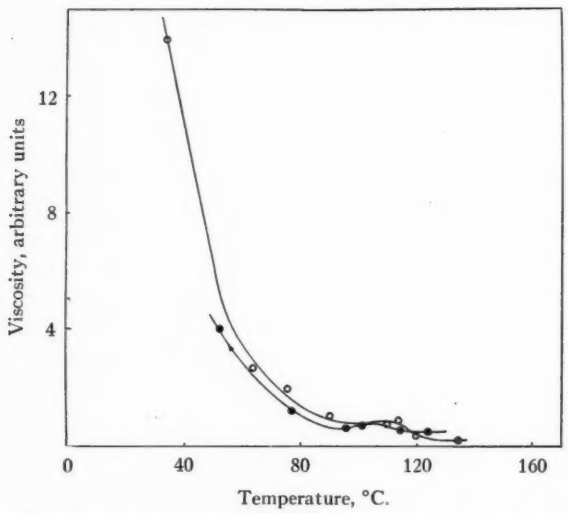

FIG. 6. *Viscosity–temperature relations of 3% calcium stearate in a 900 vis. 40 V.I. oil.*

i.e., 120° to 100° C., it was noted that the system was markedly dilatant. Even at this low concentration, the resistance to flow increased appreciably with increasing pressure at the same temperature.

Fig. 7 shows results obtained with the 10% suspension in 40 V.I. oil (large-bore capillary). On heating there is obtained first the decrease in viscosity due to the effect of temperature on the oil. At about 110° C., the viscosity rises quite sharply to a maximum at about 130° C., following which there is a decreasing viscosity with higher temperature. This dispersion was then

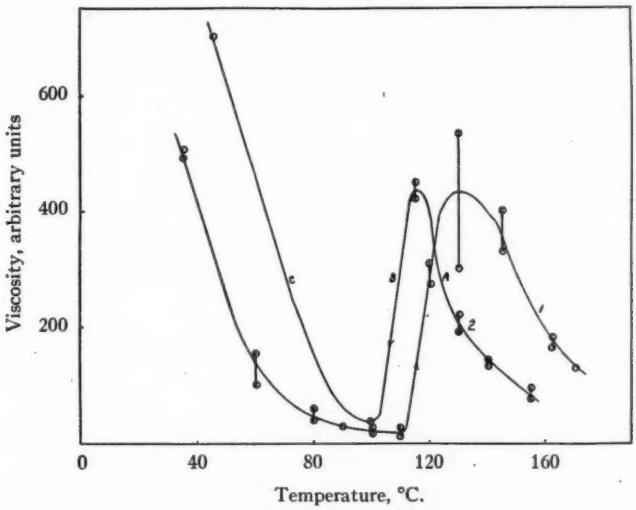

FIG. 7. *Viscosity–temperature relations of 10% calcium stearate in a 40 V.I. oil.*

maintained at 155° C., for an overnight period, following which measurements were made during cooling. The maximum was now found at about 115° C., and the minimum viscosity at about 100° C. The mineral oil had been subjected to high temperatures for a considerable period, and it is quite probable that some acid formation took place. It was noted in this connection that this dispersion showed little indication of dilatancy on cooling, and this was related in subsequent work (8) to the quantity of organic acid present. In qualitative experiments in a beaker, using a stirring motion with a spatula to judge the consistency, it was clearly shown that with repeated cycles of heating and cooling, the dilatancy decreases somewhat with each cycle in calcium-soap–oil systems showing this phenomenon. The vertical lines at points on these curves show in a relative manner the amount of change of viscosity with pressure over the range measured. It is noted that this dependence on pressure is particularly marked at the viscosity peak in each curve.

Similar results were obtained in other determinations at 10% soap concentration, and also at 15% soap concentration, where a maximum viscosity was noted at 140° C.

Fig. 8 shows results obtained with a 5% suspension of vacuum-dried calcium stearate in a 40 V.I. oil (small-bore capillary). The difference in the viscosity–temperature curve brought about by the removal of the water is immediately apparent. After the partial melting of the soap at about 105° C., there is a

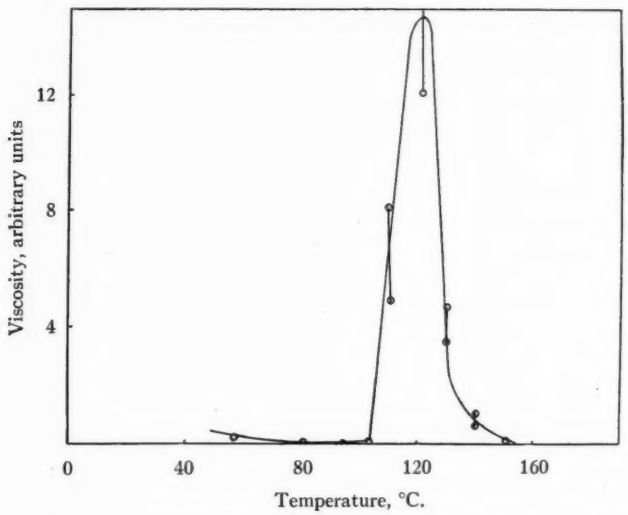

FIG. 8. *Viscosity–temperature relations of 5% vacuum-dried calcium stearate in a 40 V.I. oil.*

very steep rise in viscosity to a maximum at about 120° C., following which there is a steep decrease in viscosity to a value at 150° C. as low as that of the original "unswollen" suspension. The maximum viscosity obtained is very high for a 5% soap concentration, and the viscosity changes are very sharp. The degree of dilatancy in this system was very high virtually throughout the high viscosity range. The degree of viscosity variation with pressure is shown as before in a comparative manner by the vertical lines. A 10% suspension of the vacuum-dried soap showed similar results. A comparison of Figs. 6 and 8 shows the effect of water on the initial viscosity at low temperatures, resulting from agglomeration of suspended particles.

It is noted therefore in a comparison of the air-dry and vacuum-dried soap, that the presence of water lowers the viscosity maximum, and decreases the dilatancy. This was further corroborated in experiments where viscosity–temperature data were obtained with suspensions of carefully dried soap and then also after an excess of water was added.

Results similar to those shown above were obtained in viscosity determinations using a torsional viscosimeter, in place of the efflux type described.

The general progress of the viscosity–temperature curve of a calcium stearate suspension in mineral oil is strikingly shown by the following simple

procedure. A suspension of the soap in a 40 V.I. oil is heated to about 160° C. to effect a thorough dispersion, and a quantity is then transferred to the blade of a spatula which is held in an inclined position so as to allow the dispersion to flow. There is first noted a rapid flow due to the high temperature. The speed of flow then decreases markedly (as the viscosity reaches the maximum), then proceeds more rapidly, and finally more slowly again. These stages correspond to Sections A, B and C, shown on Curve 2 of Fig. 7.

The degree of dilatancy obtained in such systems is very great. A 25% dispersion of calcium stearate in oil at about 140° C. when at rest had the consistency of a thick molasses. When the dispersion was slowly agitated, the material clung completely to the blades of the stirrer like a solid. When agitation was stopped, the material flowed off the stirrer as a viscous liquid.

Dilatancy may be considered in some respects the opposite of structural viscosity. With the latter, the viscosity decreases with increasing pressure until Newtonian flow is attained, whereas with dilatancy, the viscosity increases with increasing pressure to a maximum which depends on the dispersion. Structural viscosity involves a streamlining of anisodimensional particles, whereas dilatancy must involve the formation of a structure which hinders flow. Dilatancy has been investigated chiefly in starch (1, 2) and silica suspensions (1), and it has been shown that it occurs only where there is a minimum of attraction among suspended particles. Dilatancy is associated with a low sedimentation volume (1, 3), and generally also with a corpuscular shape.

It has previously been shown (7) that water brings about a large sedimentation volume and a flocculation of particles of calcium stearate in oil. Dilatancy is removed by the addition of water. It is apparent, therefore, that the particles of a dry calcium soap dispersion at temperatures of 110-130° C., are independent and show no tendency to agglomeration, and that the presence of water destroys dilatancy by effecting such agglomeration.

Acknowledgment

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THE RECRYSTALLIZATION OF CALCIUM SOAPS IN MINERAL OILS[1]

By Wilfred Gallay[2] and Ira E. Puddington[2]

Abstract

The effect of various factors on the stability and physical properties of suspensions of recrystallized calcium stearate is shown. Non-polar oils form lyophobic systems that are unstable. Polar oils yield suspensions that are stable and lyophilic in character with little or no rigidity.

The effect of small quantities of water is very marked. As a result of agglomeration, a structure is developed, and the system shows a strong stream double refraction. Lower alcohols have a similar effect. Fatty acid brings about agglomeration also but increasing quantities produce a solvent effect.

Calcium oleate behaves similarly to calcium stearate, but the linoleate shows less stability.

When a calcium stearate suspension in mineral oil is heated, a sudden increase in viscosity is noted at about 100° C. This so-called "swelling" of the soap has been shown (4) to result from a partial melting of the soap to a mesomorphic state. With further heating, the degree of dispersion increases until a transparent sol is obtained. The temperature necessary to attain this state depends on the unsaturation of the soap, the nature of the oil, and the presence of various solvent factors. On cooling the highly dispersed sol, there may be obtained, depending on the above factors, a wide range of physical properties with the same soap concentration, e.g., (*a*) a smooth grease of short texture, (*b*) a thickened oil of low consistency, (*c*) a thickened oil of grainy texture, (*d*) pieces of coagel with free oil, changing on standing to a complete separation of hardened soap and free oil.

The observations made in microscopic examination of these recrystallized dispersions would appear to relate well to the stability and texture noted. There were observed in various dispersions relatively large, highly birefringent crystals with a small length–diameter ratio, long silky needles with a fine unresolvable birefringent background, and in some instances a field that was almost completely isotropic. Generally speaking, in those instances where the dispersion was unstable and separation of free oil was evident, a large proportion of relatively large isodimensional particles were noted. In stable systems that showed a considerable degree of structure and rigidity, the dispersed phase consisted essentially of the relatively longer fine fibres. The absence of doubly refracting particles was commonly observed in those products that resembled thickened oils of high viscosity. It was apparent also that the rate of cooling was important from the point of view of the crystal size. The microscopically visible particles constituted in all

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probability only a portion of the dispersed phase, but it is reasonable to assume that this portion was in general representative of all the suspended material.

The effect of several factors on the stability and physical properties of the recrystallized soap–oil suspensions was investigated.

Mineral Oil

With relatively non-polar mineral oils, as represented for example by viscosity indices ranging from 70 to 95, it was necessary to heat the suspension to about 180° C. to obtain a well dispersed sol. On cooling, the soap separated in coagel form with further syneresis to a relatively coarse suspension. In such a system, the soap recrystallizes to a form that is incapable of holding oil. The dispersion is essentially lyophobic at lower temperatures.

With more polar mineral oils, e.g., viscosity index of 40 or less, calcium stearate dispersed to a clear sol at about 110° C. On cooling, the recrystallized dispersion showed good stability. No separation of oil was noted after storage for considerable periods. The texture was smooth, denoting a relatively small particle size. The rigidity or yield value was low. The dispersion showed no loss of stability on melting to a sol of low viscosity and recooling.

The effect of polarity of the oil was further clearly shown by the following phenomenon. A relatively polar oil of 28 V.I. was extracted with acetone and the extract recovered. A marked difference between the extract and raffinate was found in the stability of their calcium stearate suspensions. The raffinate yielded a recrystallized dispersion of lesser stability.

The effect of rate of cooling on the properties of these systems was studied. For rapid cooling, the suspensions were allowed to cool directly in the laboratory to 75° F. For slow cooling, the suspensions were placed in an oven so regulated that the temperature decreased uniformly at the rate of 10° C. per hr. Little difference was noted in the stability of the dispersions with rapid and slow cooling. The smaller crystal size obtained with rapid cooling yielded a dispersion that possessed a higher viscosity for the same soap concentration. It is interesting to note that the rate of cooling has a considerably greater effect in the recrystallization of sodium soap suspensions.

Soap

Calcium oleate and calcium soaps of mixed fatty acids showed results similar to those of calcium stearate. The stability of the recrystallized dispersion decreased with decreasing polarity of the oil. It was noted that calcium oleate dispersions were particularly sensitive to slight changes of acidity, from the point of view of the stability of the system. Calcium linoleate was prepared by reacting linoleic acid with calcium hydroxide and driving off the water produced. The recrystallized calcium linoleate dispersions showed a lesser stability and lower viscosity than those prepared from the oleate or stearate. This relation is of considerable importance in

industrial applications, since the fatty acids of such oils as cottonseed and soy contain over 50% of linoleic acid, as compared with beef or mutton tallow, which contain only 5% of their fatty acids in the form of linoleic.

Calcium soaps prepared from mixed fats were suspended in mineral oils and recrystallized dispersions prepared. The stability was poor in comparison with soaps from fatty acids. In other experiments, the addition of glycerol to dispersions of calcium soaps of fatty acids was shown to effect a considerable decrease in viscosity in the recrystallized system.

Water

Calcium soap lubricating greases are all formulated with water, the amount of added water depending mainly on the presence of glycerol and the acidity of the soap used. The proportion may range from 0.1 to 3% in various systems. A relatively non-polar oil is required for a high viscosity, and it is recognized that water is necessary to provide stability in these recrystallized soap dispersions. The water is added during manufacture as the previously heated soap–oil mixture cools to just below the boiling point of water. Calcium soap appears unaffected by water even at the boiling point, and therefore the action of water in bringing about stability in the soap–oil dispersions was further investigated.

The hydrated system in a high V.I. oil shows a high degree of plasticity and a marked yield value or rigidity. The same dispersion without water is so fluid as to flow from a container, and on standing, separation of soap and oil takes place. Microscopic examination between crossed Nicols showed a distinct general difference due to the water. In the non-aqueous systems, a field of very small particles was observed. These were moderately bright or sometimes only faintly seen. The superficial appearance, owing to the size of the particles, is that of a general background of moderate brightness. In recrystallized dispersions containing water, however, larger particles were observed which showed a much greater degree of double refraction. It would appear also that there is a tendency towards a more anisodimensional form in the hydrated systems. Figs. 1 and 2 show photomicrographs of an anhydrous and hydrated system, respectively, using the same light source and magnification.

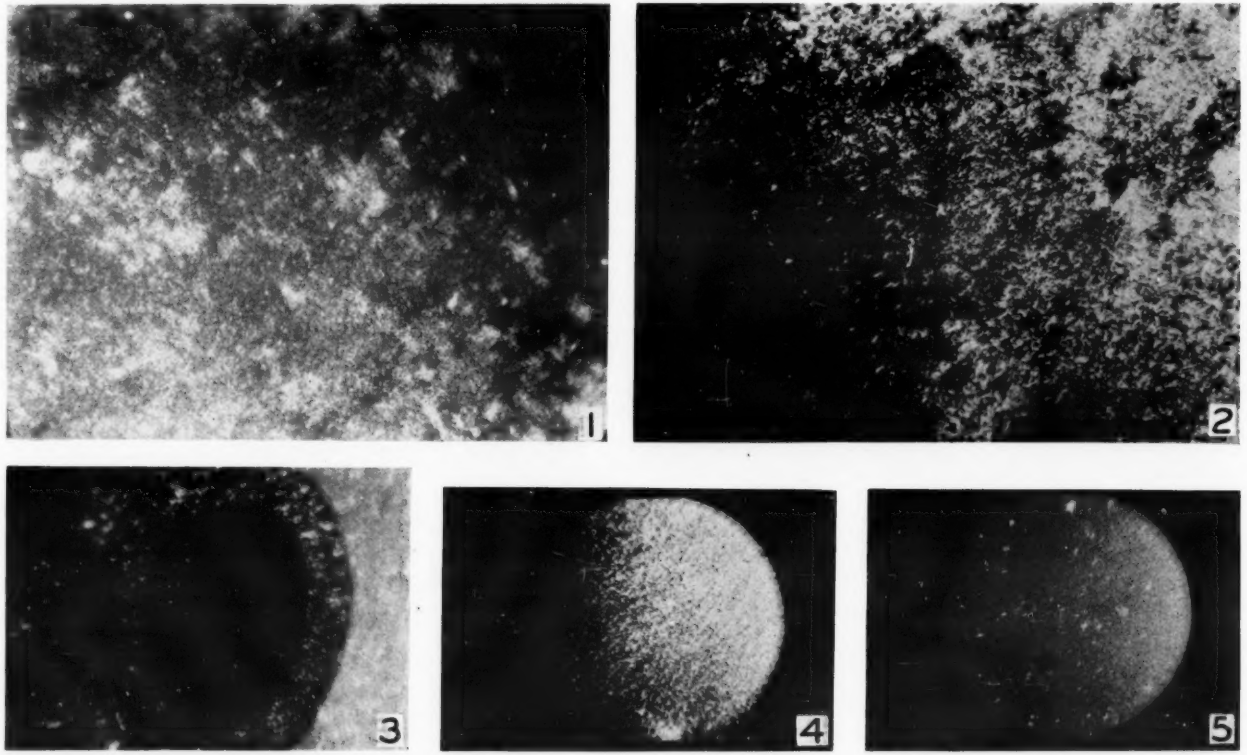
Double refraction may be induced in some systems by applied forces, which may be mechanical, electrical, or magnetic. In a gel, for example, there might be noted double refraction resulting from any or all of the following: (i) intrinsically by virtue of the doubly refracting nature of each particle, (ii) orderly arrangement of the particles, (iii) applied mechanical stresses. In a sol (i) or (iii) might be operative. Stream double refraction is the term applied to the orderliness brought about by shear stresses applied to a dispersion causing flow. The particles of dispersed phase are orientated with the long axis parallel to the direction of flow. Generally this is observed with rod-shaped particles such as in a vanadium pentoxide sol. A 5% suspension of Wyoming bentonite in water also showed a good degree of stream double

refraction, although the individual particle consists of parallel layers of platelets.

For the qualitative observation of stream double refraction, the sample was sheared by hand between two glass plates. A suitable optical system was arranged with mirrors and prisms so that a strong beam of polarized light could be passed through the plates and analysed. In this apparatus, a suspension of diatomaceous earth in oil showed no effect. A sodium soap dispersion in oil prepared in situ from oleic acid showed no stream double refraction, whereas a similar dispersion prepared from stearic acid showed an appreciable effect. It was previously shown (2) that the oleate dispersion consisted essentially of large spherical crystal bundles whereas the stearate consisted of fine short rods. It would be expected that only the rods could be orientated by a stress to show the effect. The results obtained on heating a hydrated calcium soap dispersion in oil were of interest. For these experiments, the glass plates were replaced by quartz, and the apparatus was so arranged that the material was heated by a small hot plate while under test. At elevated temperatures, the stream double refraction disappeared, and returned again on cooling. This temperature of disappearance was measured approximately by means of a surface thermocouple, and was found to be about 95° C. This coincides with the bidimensional melting point of the soap (4), and in analogy with the sodium soap (1), it might be expected that the double refraction is nil when a sufficient degree of melting takes place.

An anhydrous recrystallized suspension of calcium soap in oil showed no stream double refraction whereas the hydrated system exhibited this property to a marked degree. In order to study this effect further, an apparatus was devised to yield approximate quantitative results. The sample under investigation was placed between two glass plates, and a shearing stress was applied by moving the plates relative to one another by the fingers. The light source was a carbon arc lamp and polaroid discs were used for polarizer and analyzer. The light transmitted through the sample was measured by a photoelectric cell attached to a galvanometer with 1 ohm shunt. The highest figure recorded by the galvanometer during continued shearing was noted, and termed the stream double refraction value. The maximum reading on the galvanometer was 10 units. The precision of this apparatus was obviously not great, but the agreement in check determinations was good. Table I shows results obtained on samples taken from six lots of calcium soap dispersions in oil of commercial manufacture, (i) before addition of water, (ii) after the addition of water, (iii) after subsequent addition of a further quantity of mineral oil.

It is noted that the addition of water increased markedly the stream double refraction value of the recrystallized dispersion. Using the same apparatus rendered more sensitive by the substitution of a 100 ohm shunt for the 1 ohm shunt, the value for Batch No. 2 was still 0 before water addition, but the galvanometer needle was sent completely off the scale after the addition of water. The further addition of oil had no important effect.



FIGS. 1 AND 2. *Photomicrographs of anhydrous (Fig. 1) and hydrated (Fig. 2) calcium soaps in a 70 V.I. oil* FIG. 3. *Photomicrograph of a water droplet and agglomerated calcium stearate particles.* FIGS. 4 and 5. *Calcium soap dispersions in oil: Fig. 4, hydrated; Fig. 5, anhydrous, containing 1% of butyl cellosolve.*

TABLE I

EFFECT OF WATER ON STREAM DOUBLE REFRACTION OF CALCIUM SOAP DISPERSIONS IN OIL

Batch No.	Stream double refraction value		
	Anhydrous	Hydrated	After oil dilution
1	3	8	7
2	0	8	9
3	2.5	9.5	7
4	0.4	> 10	9
5	0	> 10	9
6	1.2	10	9

A sample of hydrated calcium soap dispersion, after storage for an extended period in the laboratory, showed a value of 5.5. After heating overnight to 82° C., the value was reduced to 1.5. Three samples of hydrated recrystallized dispersions all showed values of about 10. After heating to 85° C. overnight, values of 3.5, 1.5, and 5.5 were obtained. It is apparent that the loss of water by evaporation results in a decrease in the stream double refraction. It was shown that the addition of as little as 1% of water (based on the soap) to a calcium soap dispersion in oil increased the stream double refraction value appreciably.

Two samples were taken from a hydrated recrystallized dispersion of calcium soap in oil, and spread out in a thin layer on glass plates. One of these was placed in a vacuum desiccator over phosphorus pentoxide at 35° C., and the other was allowed to stand as a control. After several days, the treated sample showed an appreciable loss in viscosity and rigidity, whereas the control sample was essentially unchanged. Two further samples were placed in weighing bottles, one covered (i) and the other uncovered (ii), and heated to 80° C. overnight: (i) showed little change and the stream double refraction was retained; (ii) had a thin crust of separated soap and showed a marked decrease in viscosity and rigidity. The stream double refraction value was markedly decreased. Loss of viscosity and structure was noted also after hydrated samples were heated in sealed tubes to 115° C. and cooled. It is apparent that the water is not redispersed.

These data show clearly the effect of water in bringing about an alteration in the properties of the soap such that an orientation under mechanical stress is made possible. It is interesting to note that the double refraction brought about by flow was retained on stoppage of the movement so long as pressure on the sample between the plates was maintained. The relation between the stream double refraction value and stability is discussed in a later section.

Water has been shown to bring about agglomeration of calcium stearate particles in oil suspension, in determinations of sedimentation volume and attendant properties (3). Direct evidence of this effect is shown by the following experiments. A sample of a suspension of calcium stearate in a

95 V.I. oil was placed on a microscope slide and a very small quantity of water was stirred into the suspension. On stirring this system while under observation in the microscope, it was noted that layers of soap particles adhered strongly to the water droplets. When the latter were displaced by the stirring needle, the adherent soap particles moved with the water droplets as units. The experiment was repeated several times. Fig. 3 shows a photomicrograph of a water droplet and agglomerated calcium stearate particles. It is apparent that this effect becomes more important with increasing degree of dispersion of soap and of water, and therefore particularly in a recrystallized soap suspension to which water had been added near its boiling point.

Fatty Acid

The six batches of anhydrous soap dispersion noted in Table I showed considerable differences in the stream double refraction values for the same soap concentration. Analyses were carried out for free fatty acid content, and Table II shows the relation obtained. The F.F.A. is expressed as cubic centimetres of potassium hydroxide required for neutralization.

TABLE II

EFFECT OF FREE FATTY ACID ON STREAM DOUBLE REFRACTION OF CALCIUM SOAP DISPERSIONS IN OIL

Batch No.	KOH required, cc.	Stream double refraction value
2	3.3	0
5	4.5	0
4	5.3	0.4
6	5.9	1.2
1	6.0	3.0
3	6.5	2.5

It is noted that the amount of stream double refraction follows roughly the same order as the acidity, and therefore free fatty acid is also capable of bringing about to a degree an orderly arrangement of the dispersed phase leading to an increased stream double refraction. Moisture determinations on these samples by the Dean and Stark distillation method showed virtually no differences among the samples. The two batches showing no stream double refraction were also the most unstable, as might be expected from the low acidity values.

The addition of free fatty acid to calcium soap dispersions in oil lends stability to these systems on recrystallization. At the same time, the viscosity is also markedly reduced.

Since both water and free fatty acid are stabilizing agents for these soap systems, it was of interest to determine the minimum quantity of water necessary to produce stability in dispersions containing varying quantities

of free fatty acid. It is evident that there are several sources of error in such determinations, e.g., variation in the rate of evaporation and the ease of admixture of water. The dispersion was heated to 95° C. and the water was added from a micro-burette in small quantities, the end-point being judged only from the texture of a small sample after cooling. Table III shows the results obtained.

TABLE III

COMBINED WATER AND FREE FATTY ACID TO STABILIZE CALCIUM SOAP DISPERSIONS IN OIL

Batch No.	% F.F.A.	% Water required	Total F.F.A. + water, %
1	0.80	0.40	1.20
2	0.48	0.81	1.29
3	0.86	0.64	1.50
4	0.71	0.45	1.16
5	0.60	0.86	1.46
6	0.60	0.86	1.46

It would appear that there is a tendency toward the same minimum total of free fatty acid and water necessary for structure and stability. Other determinations showed that a definite minimum quantity of stabilizing agent or agents is required for each soap system.

Acid soaps are known to show a definite tendency to rancidity with time, and such rancid soaps in the case of sodium do not disperse well but form merely a gummy mass with water. The same difficulty was encountered in attempts at the hydration of calcium soap dispersions prepared from slightly rancid soaps. Dispersions prepared from neutral or slightly alkaline calcium soaps were quite stable over extended periods, e.g., several years, whereas those from acid soaps were unstable owing to rancidity and consequent loss of hydrating capacity.

Other Stabilizing Agents

A number of other reagents were tried out at their boiling points in the stabilization of calcium soap dispersions. The apparatus used consisted of the following. One beaker was sealed concentrically within another, the seal being made around the top rim. The outer beaker, acting as a jacket, led at the bottom to a tube connected to a source of boiling liquid. A side tube sealed on at the rim led to a condenser so that the boiling vapour from various liquids could be used and refluxed. In this way any desired temperature could be thermostatically maintained. The mixture contained in the inner vessel was stirred mechanically. Methyl, ethyl, *n*-propyl, and *n*-butyl alcohols were used in 1% concentration (based on the soap) at temperatures just above their boiling points. All these alcohols were found to yield recrystallized soap dispersions of excellent stability and viscosity. Since the boiling point of methyl alcohol is far below the bidimensional melting point

of the soap used, it is apparent that the action of the stabilizer is on the fully solid crystal. The degree of dispersion may be expected, however, to have an effect on the viscosity of the dispersion for a given concentration.

A number of miscellaneous types of materials were tried out for their effect on the stability of these recrystallized soap dispersions. Octyl alcohol, butyl cellosolve, butyl carbitol, and certain waxes provided stability but the texture of the dispersion was appreciably affected. With an excess of the reagent, a product resembling a thickened oil was obtained. It would appear that all such reagents lend stability through their solvent power on the soap. Figs. 4 and 5 show a hydrated calcium soap dispersion and an anhydrous dispersion after the addition of 1% butyl cellosolve, respectively. Although stability is attained, the agglomerating effect obtained with water is absent. The addition agent does not bring about a structure or rigidity in the system.

Discussion

On heating a suspension of calcium stearate in mineral oil, the soap undergoes a partial melting to a mesomorphic state (4), following which dispersion of the soap continues to an extent dependent on the polarity of the oil used. Polar oils exert a marked solvent effect above the partial melting point, and a clear sol condition is attained a few degrees above that temperature. In a relatively non-polar oil, however, such a high degree of dispersion is not attained until a considerably higher temperature is reached.

On cooling, the physical properties of the suspension of recrystallized soap in oil depend largely (*a*) on the polarity of the oil, and (*b*) on the presence of various additives. Using a non-polar oil, the system is essentially lyophobic and the suspension is unstable, the soap separating out in coarsely divided form. With polar oils, a relatively stable suspension is formed on cooling. The viscosity of the suspension is high, with virtually no yield value, typical of lyophilic systems in general. It is apparent that the polar oil thus exerts some solvent action.

The effect of water on the properties of a suspension of calcium stearate in oil is very marked. Where a non-polar oil is used, the suspension shows a high degree of stability and a high yield value in flow. Water has been shown to bring about a wetting action of oil on calcium soap (3), and has been shown also to exert a marked agglomerating effect on the suspension (3). The present work presents direct evidence of this effect. It is apparent that such an agglomeration will bring about a physical structure in the suspension leading to a marked yield value in flow. This agglomeration and structure lead also to the property of stream double refraction, denoting an orderly alignment of the structural units under a stress. No stream double refraction is shown by calcium stearate dispersions in the absence of an agglomerating agent. Other additives, principally the lower alcohols, act similarly to water in this regard. Fatty acid also brings about agglomeration of the soap, but a solvent effect is introduced with larger quantities.

Stability in these recrystallized soap suspensions is thus brought about (*a*) by agglomerating agents to provide a structure of the particles, or (*b*) by polar constituents to render the system somewhat lyophilic. The texture and flow properties of these two types differ markedly, principally in the degree of rigidity in the system.

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